



ENABLING HIGH-ENERGY/HIGH-VOLTAGE LITHIUM-ION CELLS FOR TRANSPORTATION: ELECTROCHEMISTRY AND EVALUATION

Project ID: BAT252

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Merit Review

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OVERVIEW

Timeline

- Start: October 1, 2014
- End: Sept. 30, 2018
- Percent complete: 94%

Budget

- Total project funding:
FY17 \$4.0M
- BAT252, BAT253, and BAT254
(ANL, NREL, ORNL, LBNL)

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
 - Cost
 - Performance
 - Safety

Partners

- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

PROJECT OBJECTIVES - RELEVANCE

Energy and Power loss during calendar-life and cycle-life aging limits the commercial viability of lithium-ion cells for transportation applications

- High-performing, high-energy, safe and long-life batteries are needed to reduce petroleum consumption in vehicular applications
- Performance targets of plug-in electric vehicle (PEV) and electric vehicle (EV) batteries can be met by cells containing layered-oxide-based positive electrodes
- To achieve the energy and power density targets, cells with these electrodes must be cycled to voltages that exceed 4.5 V vs. Li/Li⁺
- On extended cycling at these voltages, capacity loss, impedance rise and voltage fade reduce the cell's energy and power output
- Our goal is to examine the mechanisms associated with this loss in performance and to develop cell chemistries that enable operation over the 15 y life target set by the DOE-OVT

APPROACH

Multi-institutional effort to identify and solve performance loss problems in the high energy high voltage cells

- Identify additives, which when incorporated into our baseline electrolyte (Gen2), consisting of 1.2M LiPF₆ in EC:EMC (3:7 w/w), reduces cell degradation
 - Provide an understanding of electrolyte-additive mechanisms through closely-coupled experimental and computational techniques
- Characterize the behavior of fluorinated solvents, which are stable at high potentials (oxidation resistant) but not stable at the graphite anode (easily reduced)
 - Examine effect of highly fluorinated electrolyte on the impedance rise and capacity retention of NMC/graphite full cells using “preformed” graphite anodes
- Develop a fundamental understanding of gas generation and reactivity in the high energy high voltage cells. Insights will allow better control over SEI/CEI chemistry, improve interfacial stability, and minimize impedance rise.
 - Use FTIR and GC-MS to characterize gas composition *in situ* and *ex situ*.
- Formulate experiments to examine the various crosstalk processes during cycling
 - Identify effects of transition metals in the electrolyte on cell performance
- Advance understanding of mechanisms leading to cell impedance rise
 - Is impedance rise affected by the type of anode in the cell?

WHAT WE KNOW ABOUT CELL PERFORMANCE LOSS

Layered oxide-graphite cells: Instabilities at both electrodes

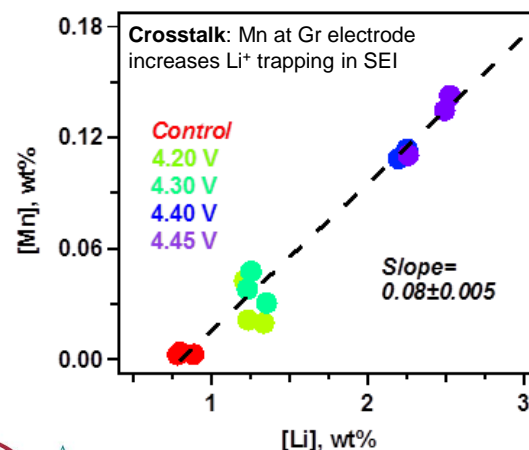
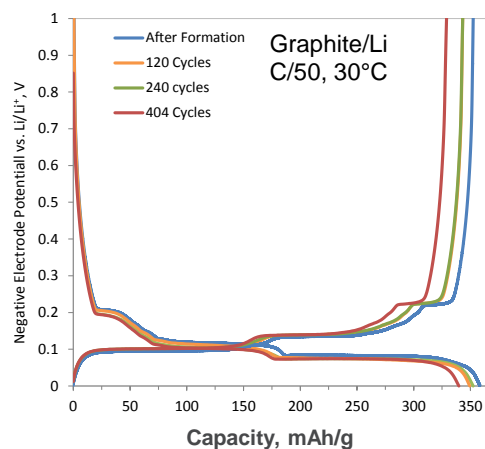
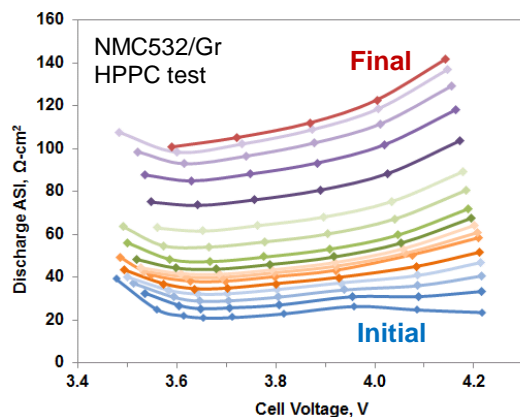
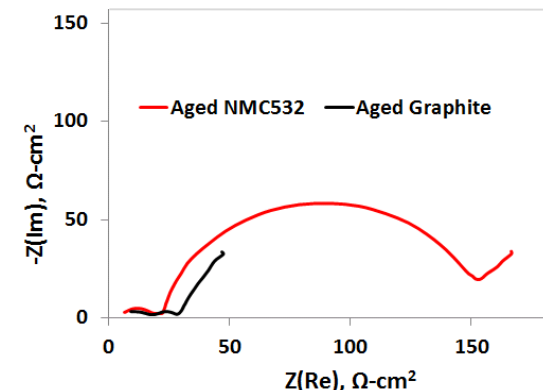
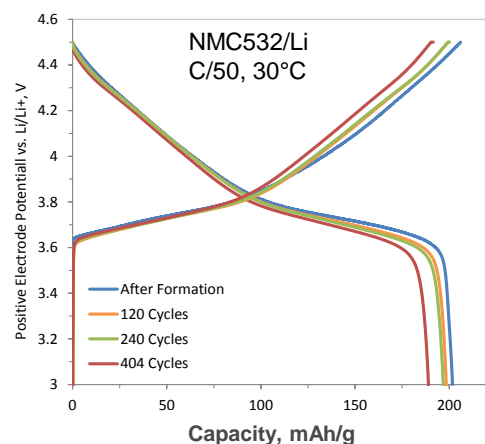
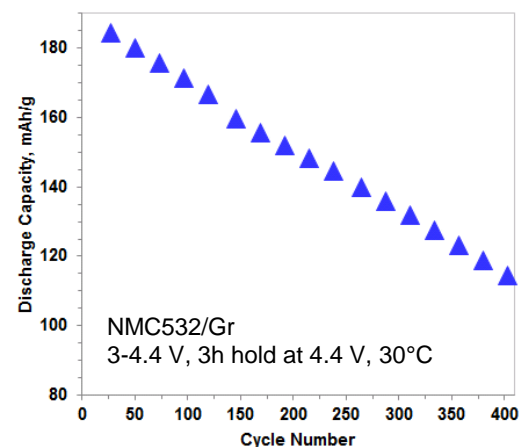
NMC/Gr cells cycled at high voltage lose capacity and power capability (impedance rise) with increasing cycle number



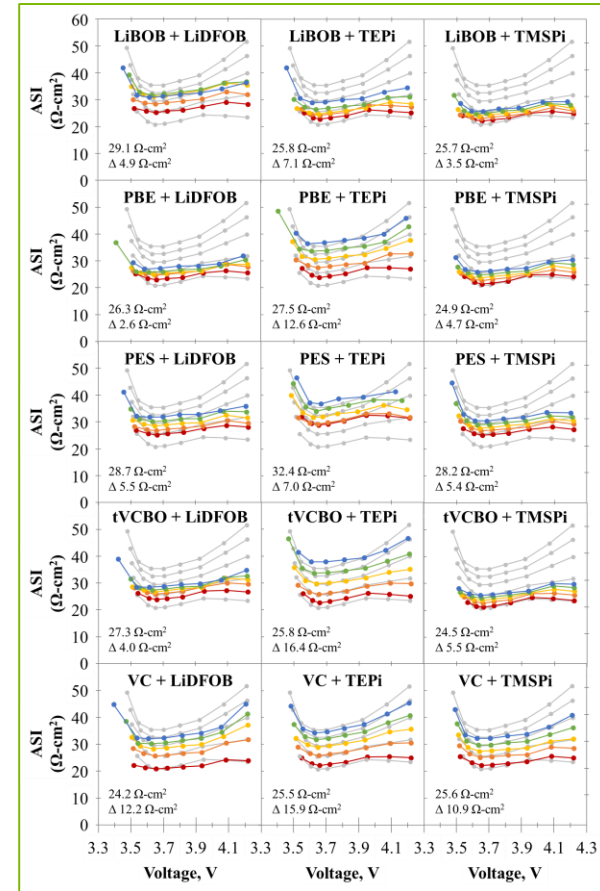
After cycling, extracted electrodes have not lost capacity → Capacity loss is due to Li-trapping (in SEI), not material degradation.



Extracted electrodes from aged cells indicate that impedance rise is from processes at the cathode-electrolyte interface

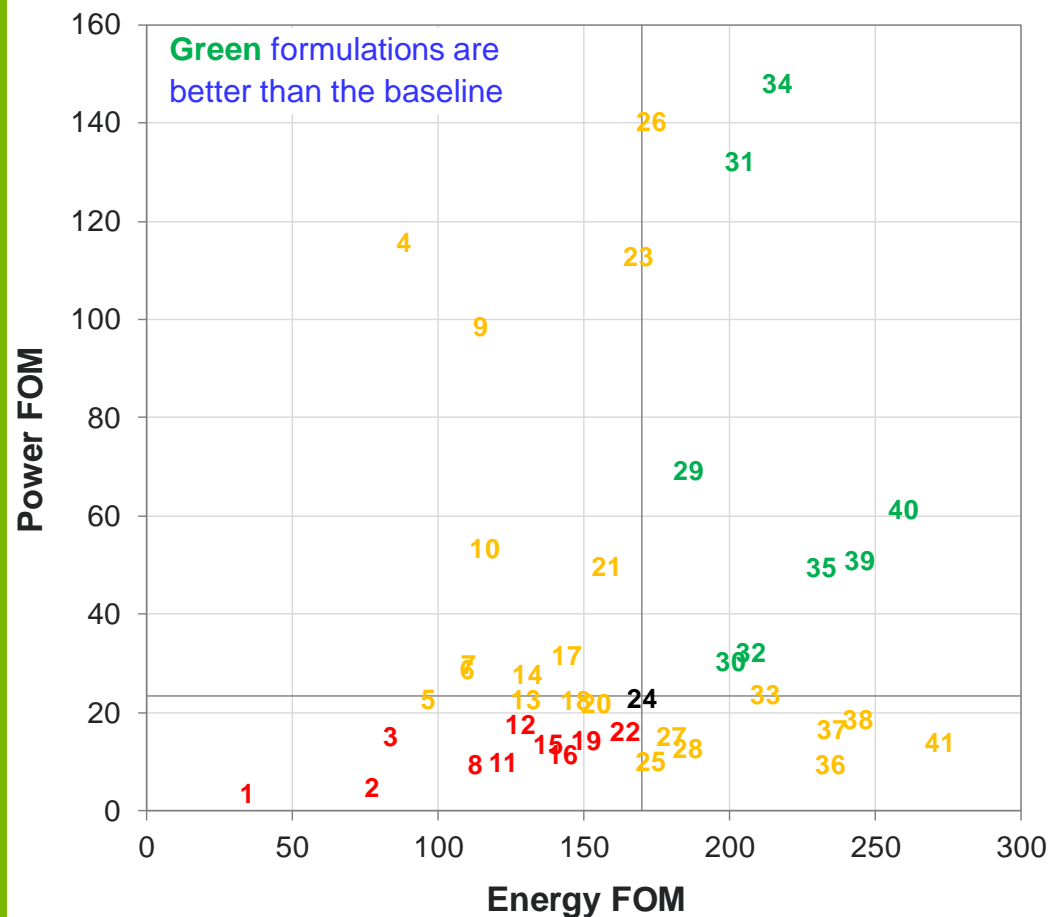


ASI vs. V as a function of aging



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FIGURE OF MERIT (FOM) METHODOLOGY DEVELOPED TO IDENTIFY PROMISING ELECTROLYTE FORMULATIONS

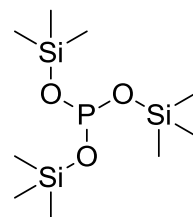


Label	Formulation	Label	Formulation
24	Baseline	41	0.5 VC & 1.0 TMSPa
40	1.0 VC & 1.0 TMSPi	38	1.0 TMSPi (2 wk old)
39	0.5 VC & 1.0 TMSPi	37	1.0 TMSPa
35	Lit Sep + 1.0 TMSPi (1 wk old)	36	1.0 TMSPi (3 wk old)
34	1.0 TMSPi (1 wk old)	33	2.0 FEC & 1.0 TMSPi (1 wk old)
32	1.0 TMSPi	28	1.0 VC & 2.0 TMSPi
31	0.2 tVCBO & 1.0 TMSPi	27	1.0 VC & 1.0 TMSPi (1 wk old)
30	2.0 VC & 1.0 TMSPi	26	0.25 tVCBO & 1.0 TMSPi (symm)
29	0.5 VC & 1.0 TMSPi & 0.5 TEPI	25	10.0 TMSPi (1 wk old)
22	Lit Sep	23	0.25 PBE & 1.0 TMSPi
19	1.0 VC & 0.5 TMSPi	21	0.25 tVCBO
16	0.5 TMSB	20	1.0 PES & 1.0 TMSPi
15	1.0 TEPI	18	2.0 VC & 1.0 TEPI
12	2.0 PES & 1.0 LiDFOB	17	2.0 VC & 1.0 TMSPi & 1.0 DME
11	1.0 LiBOB & 2.0 LiDFOB	14	1.0 VC
8	1.0 TMSB	13	1.0 VC & 1.0 TEPI
3	0.25 PBE & 1.0 TEPI	10	1.0 LiBOB & 1.0 TEPI
2	1.0 PES & 1.0 TEPI	9	1.0 LiBOB & 1.0 TMSPi
1	0.3 PCl3	7	0.25 tVCBO & 2.0 LiDFOB
		6	2.0 VC & 2.0 LiDFOB
		5	0.25 tVCBO & 1.0 TEPI
		4	0.25 PBE & 2.0 LiDFOB

The Gen2 + 1wt% TMSPi (1 wk old) electrolyte shows the highest Power FOM of the 40 different formulations studied.

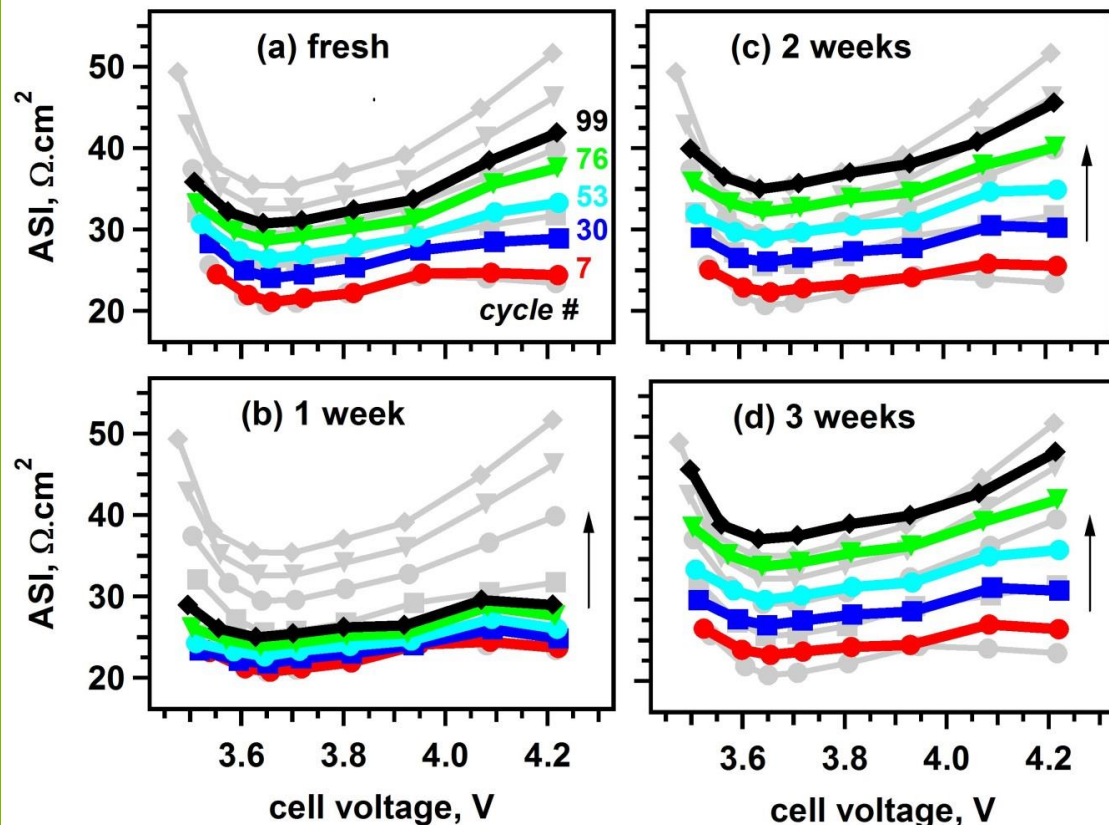
TMSPi ADDITIVE: “ELECTROLYTE AGING” MATTERS!

Lowest impedance rise for cells with “1-week old” electrolyte



NMC532/Gr, 3-4.4 V w/ 3h hold at 4.4 V

Electrolyte: Gen 2 + 1 wt% TMSPi



HPPC data

2C, 10s discharge pulse

Aging period indicated in plots

Observations

Impedance rise is lower than Gen2 electrolyte for freshly-prepared electrolyte w/TMSPi. The 1-week old electrolyte shows the slowest rise. Further aging increases cell impedance.

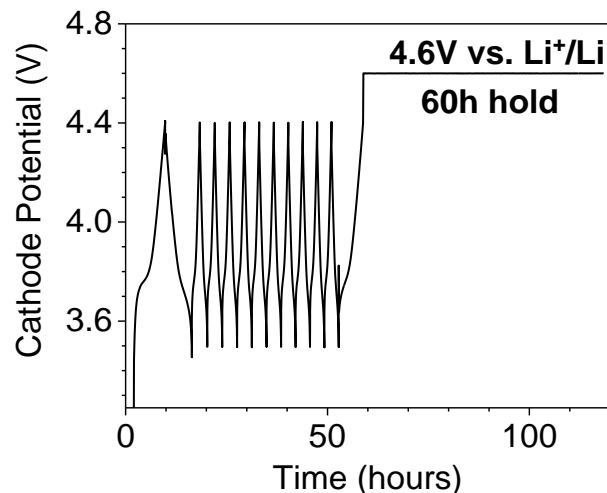
Key Takeaway

Additives can react with the baseline electrolyte to form compounds that have beneficial or detrimental effects on cell performance and aging.

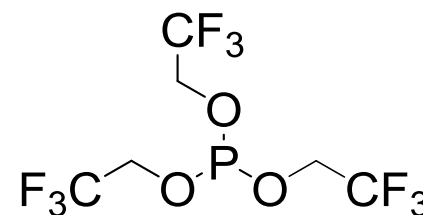
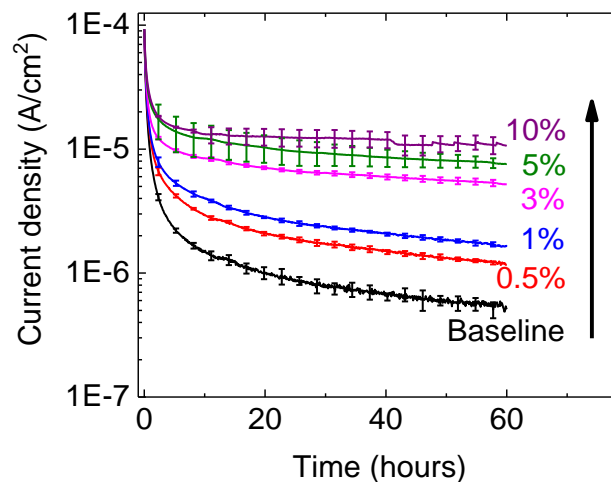
Gen 2 electrolyte (EC:EMC (3:7 w/w) + 1.2 M LiPF₆)
data shown for comparison (grey in all plots)

ELECTROCHEMICAL BEHAVIOR OF TTFP ADDITIVE

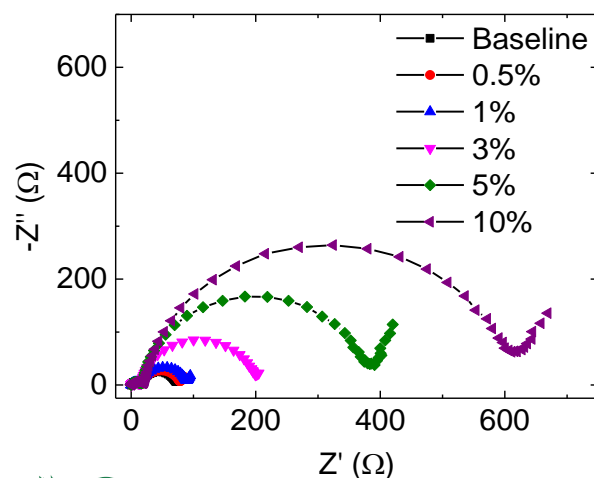
Aging protocol



Leakage current vs. TTFP concentration



Impedance vs. TTFP concentration



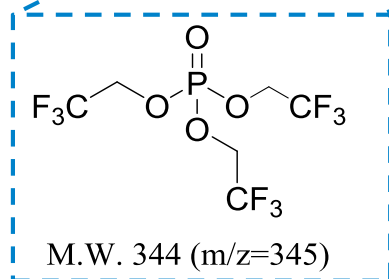
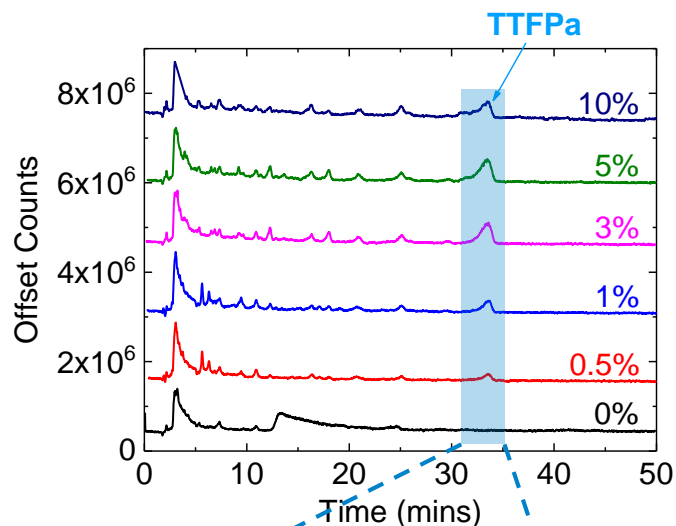
TTFP:

1. is oxidatively unstable,
2. does not passivate cathode surface, and
3. leads to higher impedance of the cathode.

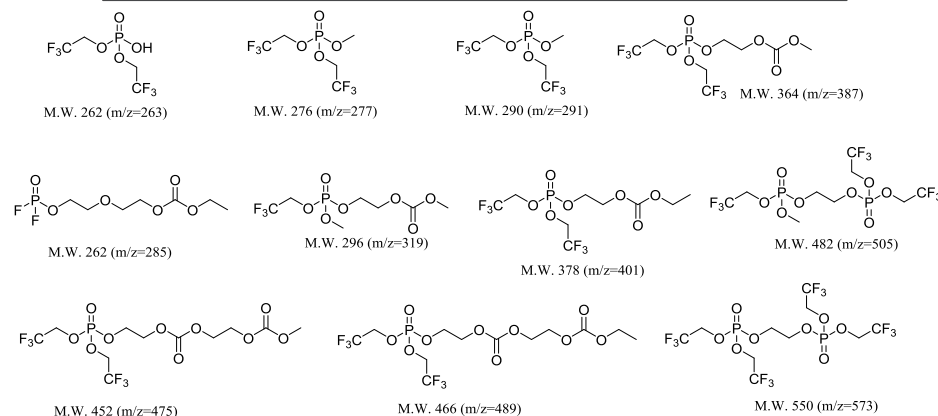
What are the chemical reactions?

TTFP OXIDIZES TO TTFPa AND FURTHER REACTS WITH ELECTROLYTE TO FORM SOLUBLE SPECIES

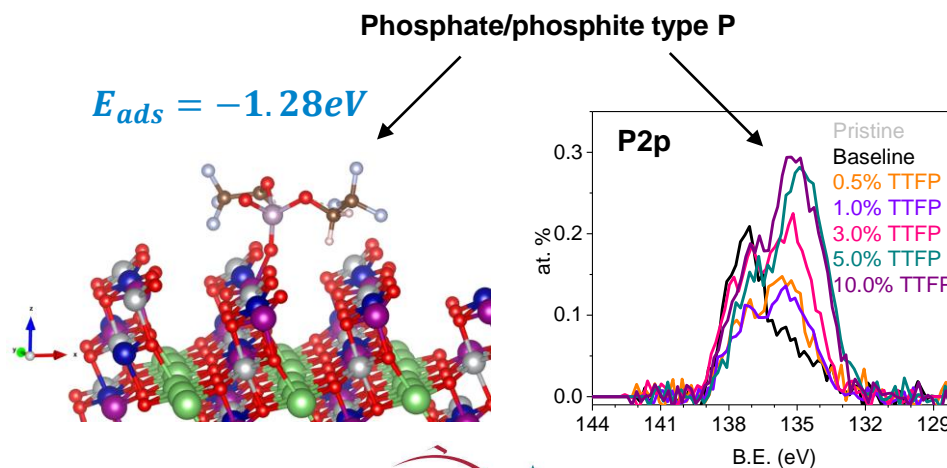
TTFP predominantly forms TTFPa via oxygen abstraction and stays in solution



Many other TTFP decomposition products detected and characterized with HPLC



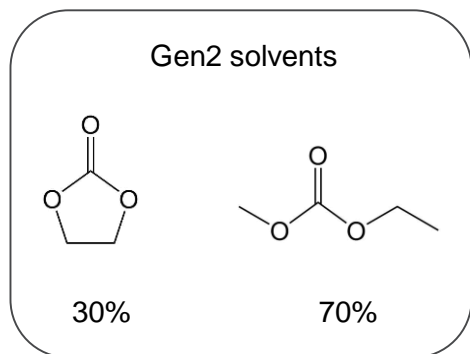
Simulations are consistent with XPS, showing some PO_x groups on cathode surface



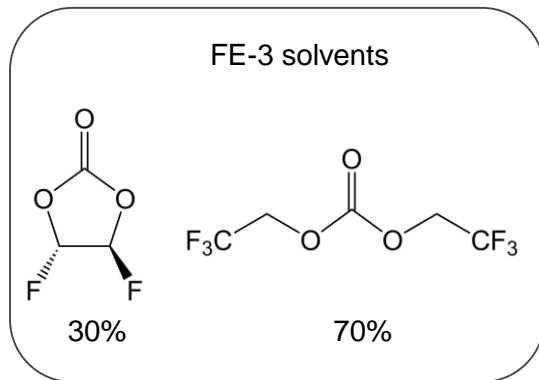
FLUORINATED ELECTROLYTES ARE STABLE AT HIGH VOLTAGE – EFFECT ON NEGATIVE ELECTRODE SEI?

How can we investigate stability on the graphite electrode?

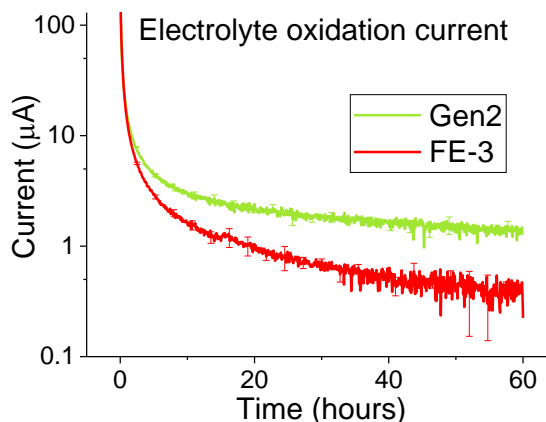
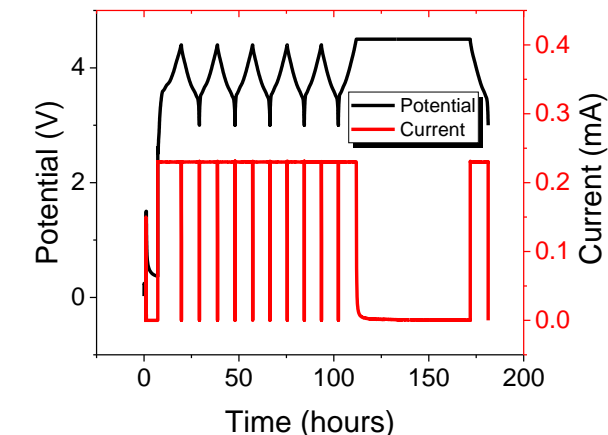
Fluorinated solvent formulation



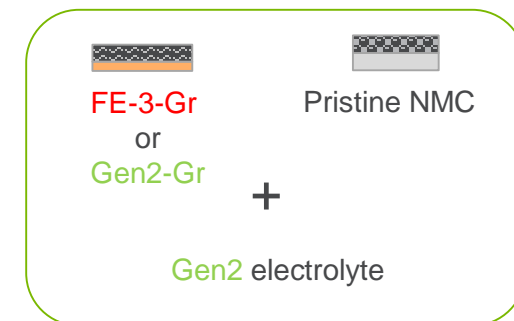
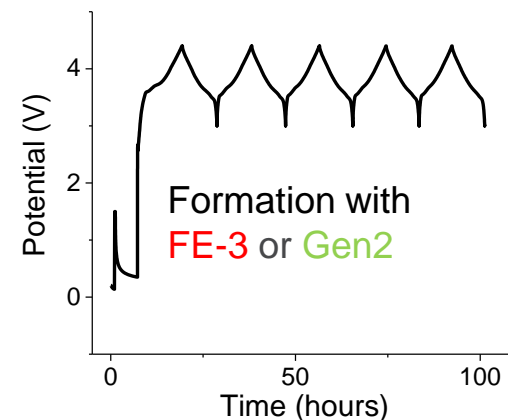
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Anodic stability evaluation with high voltage hold



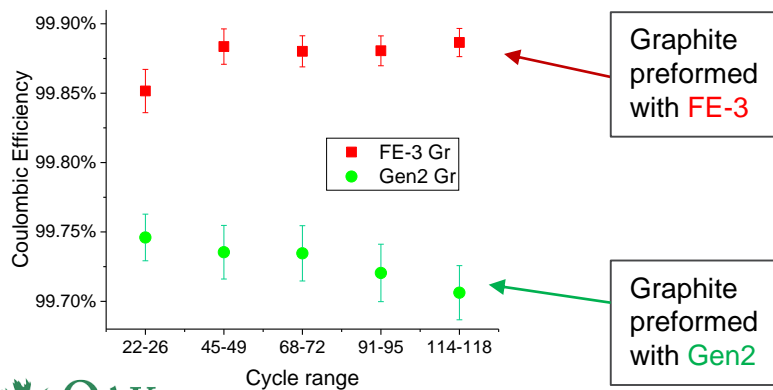
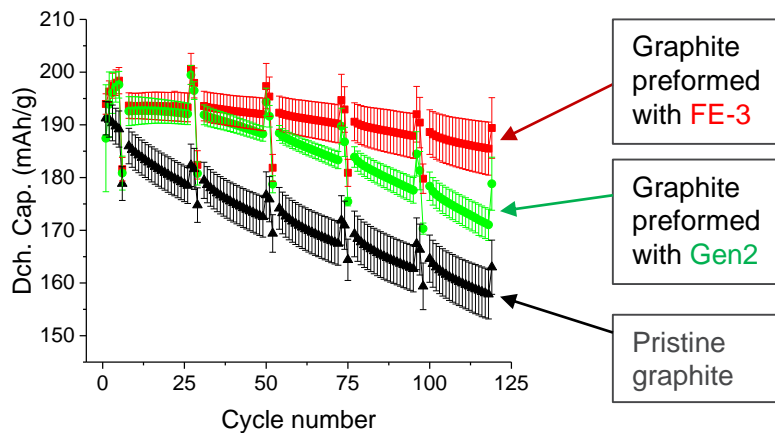
SEI stability evaluation with preformed graphite anodes



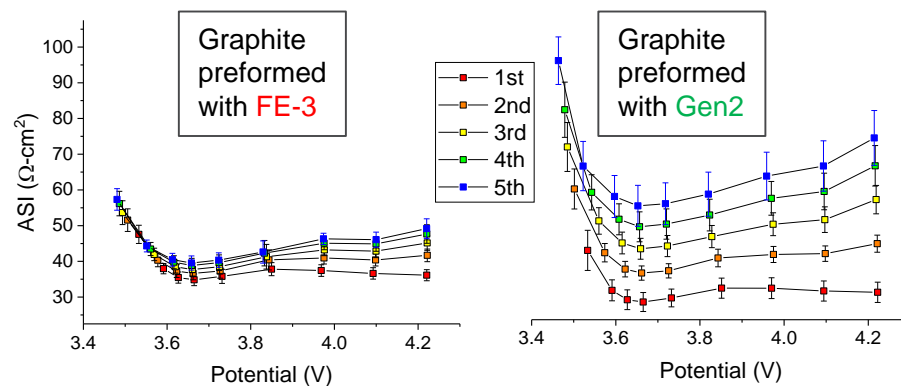
GRAPHITE PREFORMED WITH FE-3 ENHANCES BASELINE ELECTROLYTE PERFORMANCE

Baseline Gen2 electrolyte shows better stability in both cycling and impedance rise when paired with FE-3 preformed graphite

Influence of preforming electrolyte identity on capacity retention and coulombic efficiency



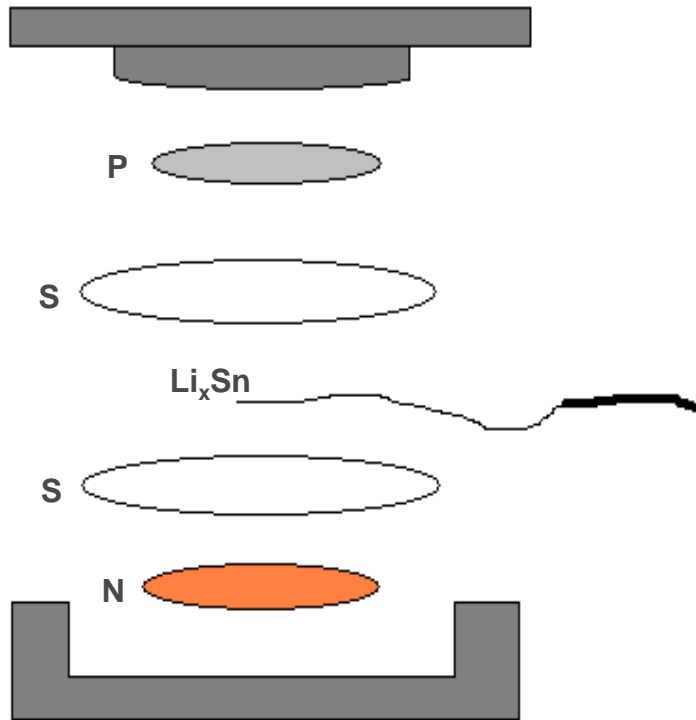
Influence of preforming electrolyte identity on impedance rise



Graphite preformed with FE-3 (FE-3 SEI) shows substantially better capacity retention and lower impedance rise

Anode SEI influence on impedance rise (cathode/electrolyte interface) indicates crosstalk is a contributor to impedance rise

IMPEDANCE EVOLUTION IN THE LAYERED-OXIDE CATHODES IS AFFECTED BY THE ANODE TYPE



Impedance data (HPPC, EIS) on full cell and individual electrodes can be obtained using this Reference Electrode setup

CAMP Electrodes, Gen2 electrolyte Potential hold at Upper Cutoff Voltage

NMC811/Gr (Positive at ~4.5 V during hold)

NMC811/LTO (Positive at ~4.5 V during hold)

NMC811/LTO (Positive at ~4.0 V during hold)

Observations

Impedance rise at positive electrode is greater for cells with $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Impedance rise at positive electrode is minimal when hold potential is 4.0 V

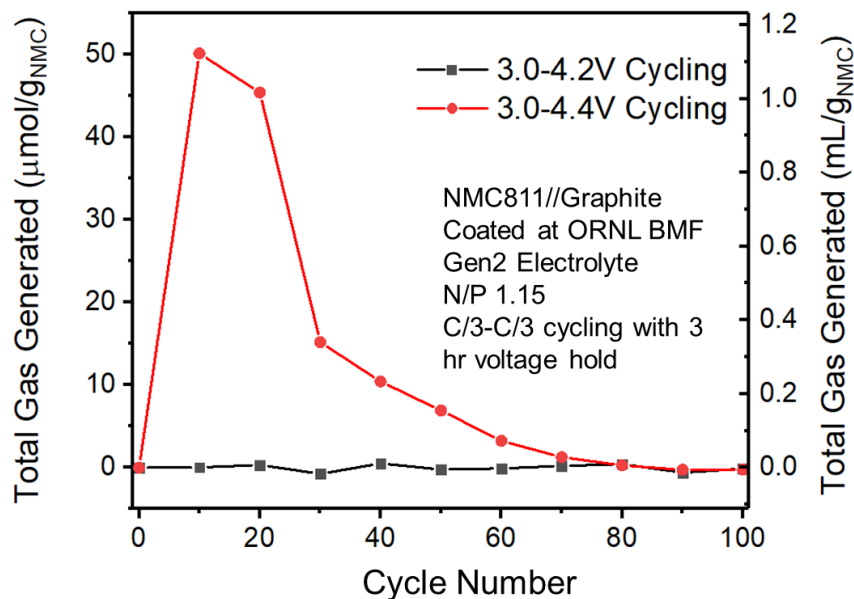
Postulated Mechanism

Accumulation of gases in cells responsible for impedance rise

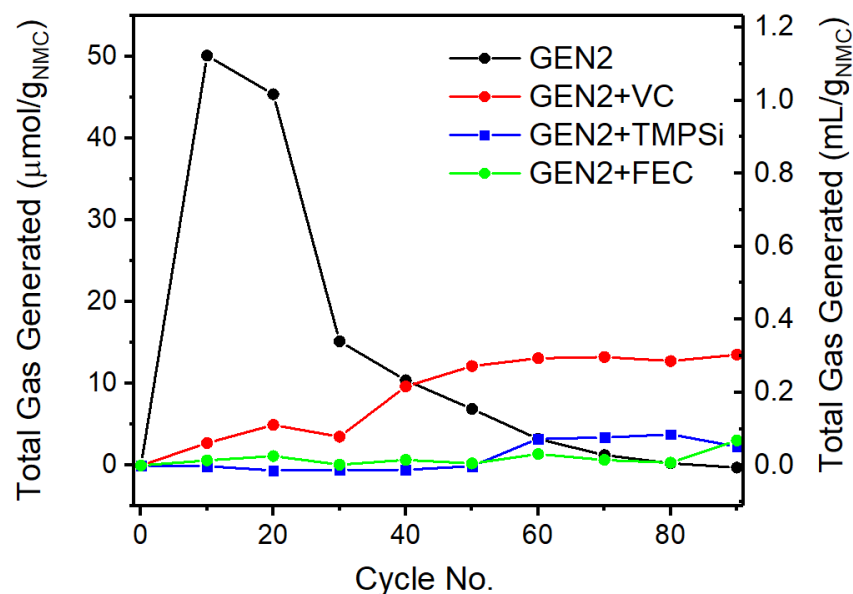
Related to gas generation at positive and depletion at negative electrode (*crosstalk*)

SIGNIFICANT GAS EVOLUTION IN HIGH VOLTAGE NMC811//GRAPHITE (POUCH) CELLS

Gas volume measured by the Archimedes method. Cycle 0 is after 4 formation cycles and degassing.



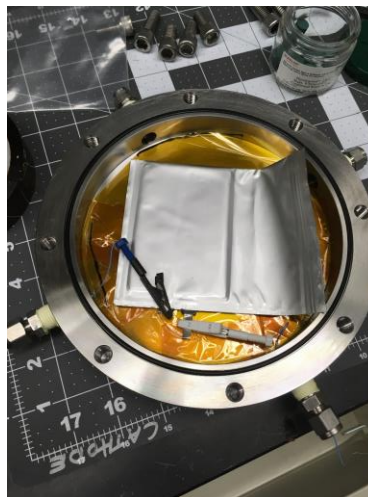
- Minimal gas generation in 3.0-4.2 V cycling window
- Significant gas generation in 3.0-4.4 V cycling window during the early cycles; gas depletion during the later cycles.



- VC, TMSPi, FEC additives (2 wt.%) change the gassing behavior.
- Additives lower gas evolution during the early cycles relative to Gen2 electrolyte.
- TMSPi additive also lowers impedance growth, confirming previous results.

AEGIS – ANALYSIS OF ELECTROCHEMICAL GASSING BY INFRARED SPECTROSCOPY

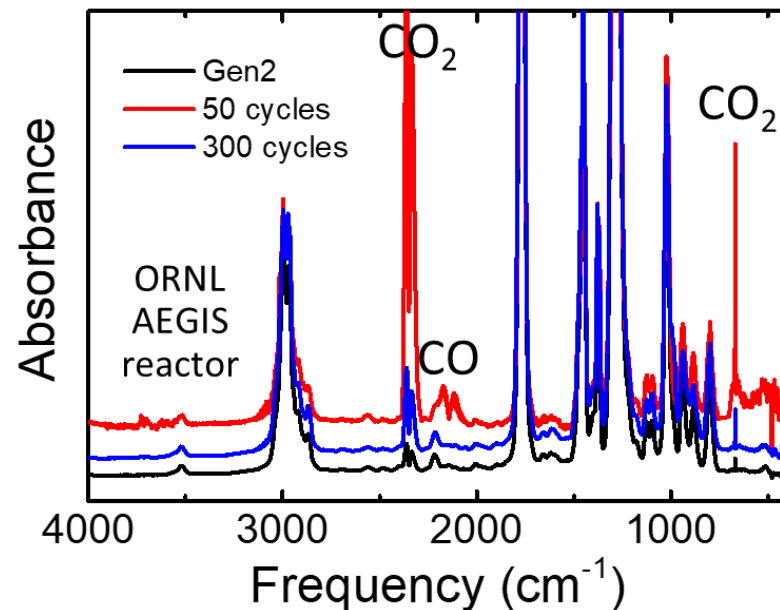
Probes the gas phase continuously with IR spectroscopy in a batch mode without drying out the cell



Reactor large enough to probe a 5 Ah battery

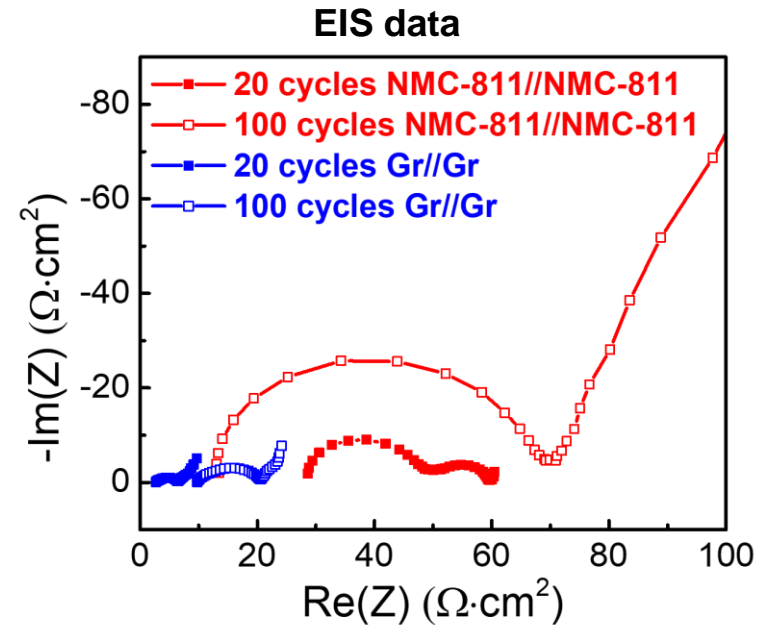
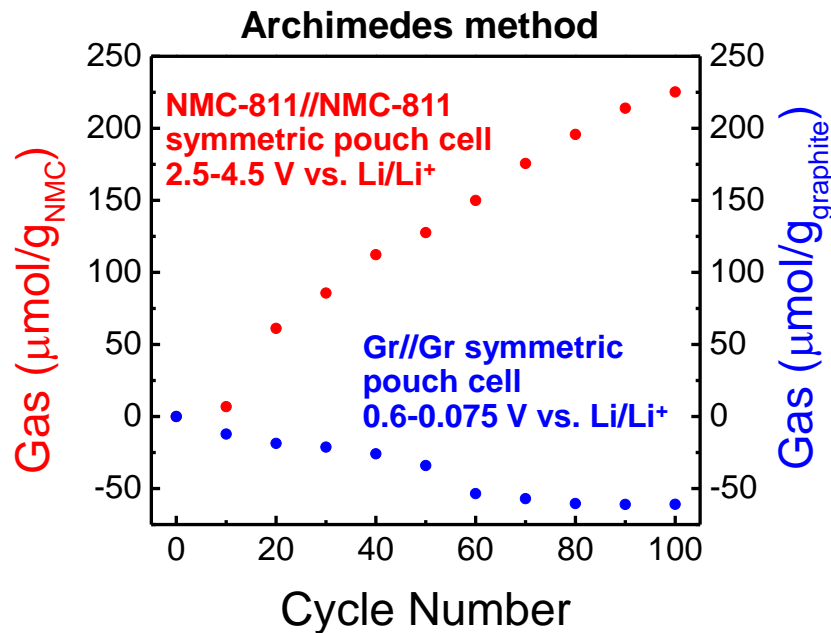
Key Observations: FTIR and GC-MS

- CO_2 , CO, alkanes, and ethers are the main gases in NMC811//Gr cells.
- CO_2 decreases with cycling; possible consumption at the anode (*crosstalk*)
- Alkanes (methane, ethane) build up during cycling.



NICKEL-RICH CATHODE MAINLY RESPONSIBLE FOR GAS GENERATION AND IMPEDANCE RISE

Symmetric Gr//Gr and NMC811//NMC811 pouch cells isolate gas formation and impedance growth at the anode and the cathode.



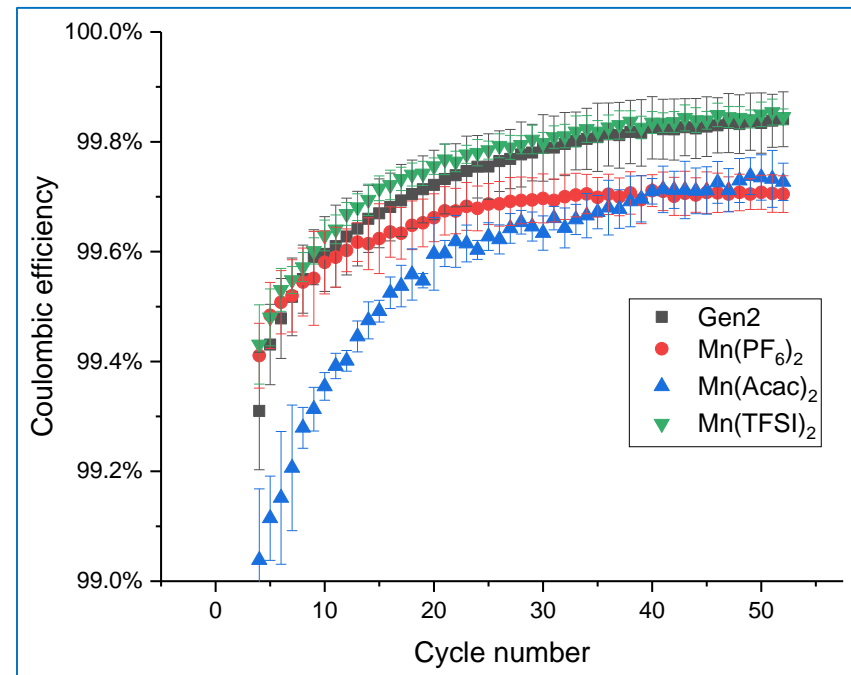
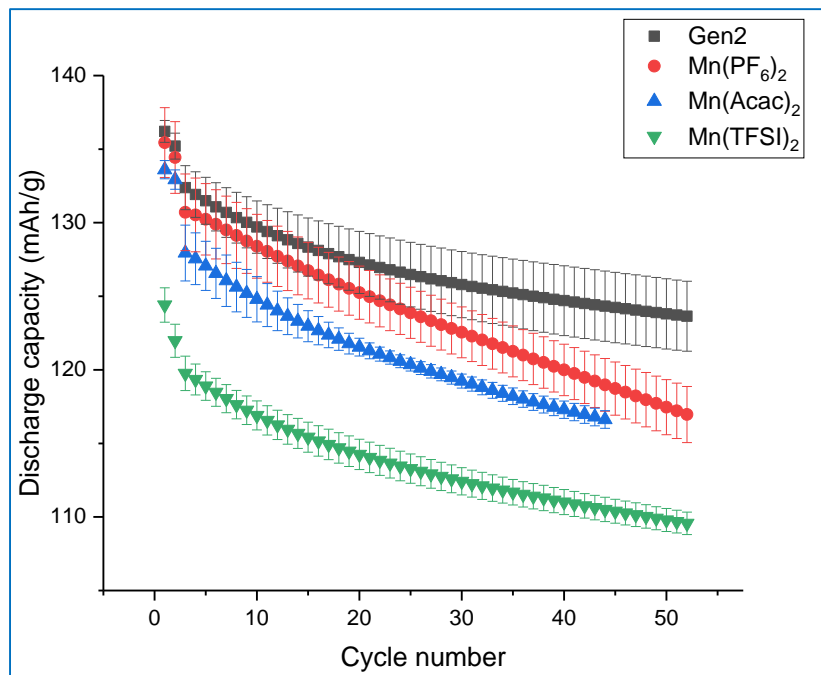
- Continuous gas (e.g. CO₂) generation in NMC-811 cell on cycling
- Gas (e.g. CH₄, C₂H₄, C₂H₆) generated in Gr cell is consumed on cycling

Impedance increase of NMC-811 cell is significantly larger than the increase for the symmetric Gr cell

Mn IN ELECTROLYTE ACCELERATES CELL CAPACITY FADE (Li⁺ TRAPPING IN ANODE SEI)

Cell capacity is affected by the nature of the anions

LiFePO₄/Gr, C/3 cycling, 1000 ppm Mn (by mass) in Gen2 electrolyte



PF₆: Continual capacity loss

Acac: Initial and continual capacity loss

TFSI: Initial capacity loss

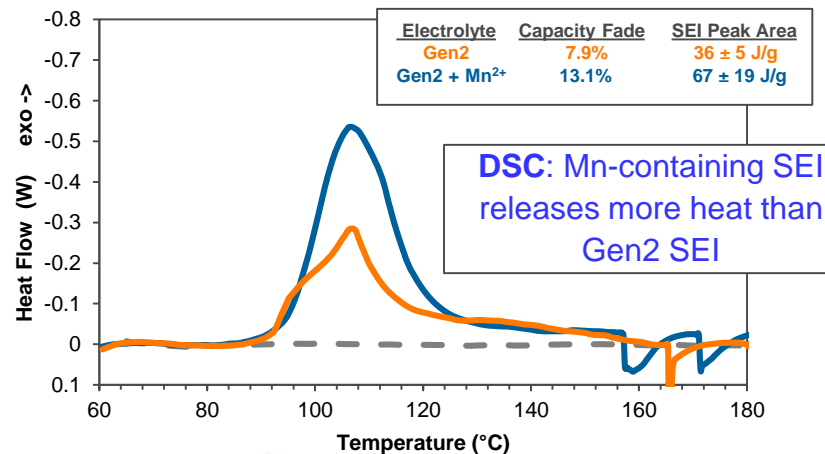
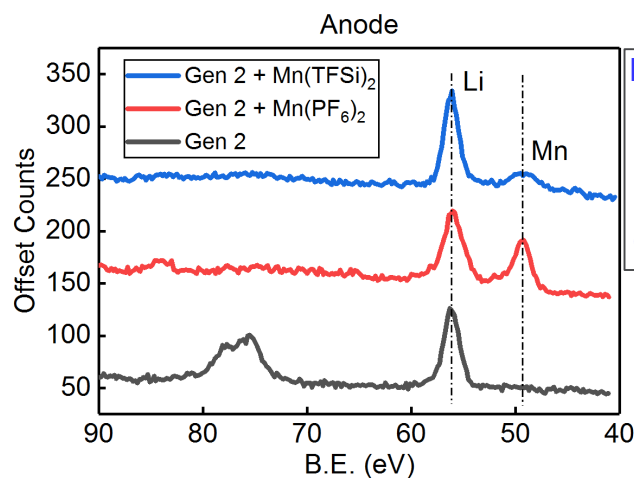
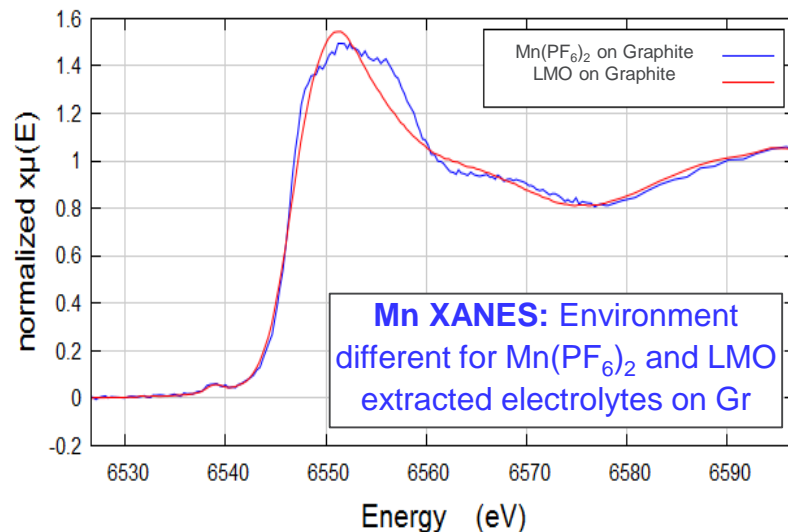
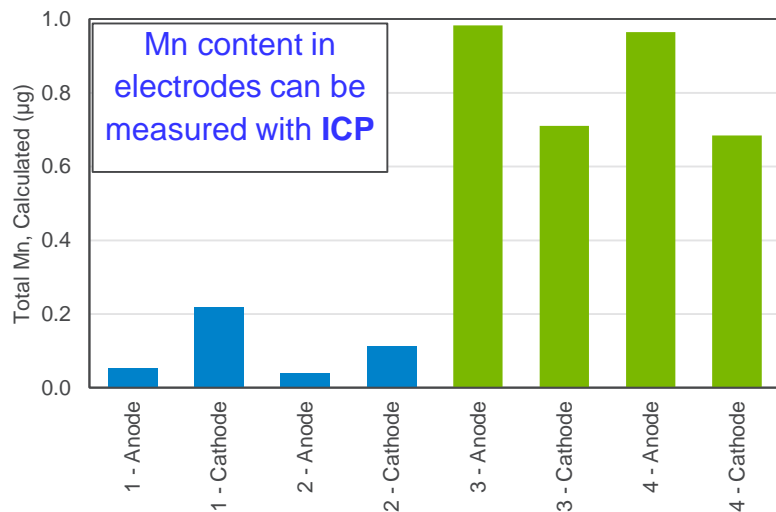
PF₆: Continual low CE

Acac: Initial and continual low CE

TFSI: No change from baseline

SPIKED ELECTROLYTES: Mn SALT IN GEN2

Characterization techniques employed to determine the chemical and electrochemical mechanisms of the various Mn environments



SUMMARY

- Developed Energy and Power Figure of Merit (FOM) criteria to identify additive systems that outperform the baseline (Gen2) electrolyte
 - Several additive combinations outperformed the baseline electrolyte i.e., had higher Energy FOM (better capacity retention) and Power FOM (lower impedance rise)
- Additives can react with the baseline electrolyte to form compounds that have beneficial or detrimental effects on cell performance and aging
 - Cells with the Gen2 + 1wt% TMSPi electrolyte, aged for 1 week, displayed the lowest impedance rise. Further aging generates products that raise cell impedance.
- Evaluated stability of graphite SEI's formed by both a highly fluorinated electrolyte (FE-3) and Gen2 baseline electrolyte
 - Graphite preformed with FE-3 shows substantially higher capacity retention, coulombic efficiency, and impedance rise than graphite preformed with the Gen2 electrolyte, indicating that anode to cathode crosstalk is a contributor to cathode impedance rise
- Gas generation in NMC811//Gr cells charged to >4.2 V is significant and correlates strongly with impedance rise and capacity fade.
 - Most gas evolution and impedance rise occur at cathode in NMC811//Gr cells. Common electrolyte additives can significantly reduce gas evolution and impedance rise in high voltage NMC811//Gr cells.
- FTIR combined with a custom-built reactor provides a non-destructive, non-invasive method to study gas evolution in high energy cells.
 - Large-format pouch cells can be studied *in situ* without “electrolyte drying” complications

FUTURE WORK AND WORK IN PROGRESS

- Connect the impact of additives on cell performance to fundamental changes in surface chemistry and gas evolution behavior
 - Mechanisms that explain the effect of these additives will be obtained using experimental and computation techniques
- Continue to develop FTIR and GC to monitor gas generation *in situ*
 - Work in progress to identify gas and molecular changes during cycling
- Understand the impact of gas crossover and reactivity on SEI/CEI chemistry and interfacial stability
 - Intentionally introduce reactive gases into cells to control the interface
- Mn dissolution from NMC oxide contributes to cell performance degradation
 - Electrolytes spiked with Mn salts and electrolytes extracted from LiMn_2O_4 -cycled cells will be evaluated in electrochemical cells
 - Characterization and post-test analysis will be conducted on electrodes after cycling with Mn-containing electrolytes
- Continue development of symmetric cell methodology for diagnostic analysis
 - Data from such cells are valuable to highlight the effect of crosstalk during electrochemical cycling of full cells

Any proposed future work is subject to change based on funding levels.

CONTRIBUTORS AND ACKNOWLEDGMENT

Research Facilities

- Materials Engineering Research Facility (MERF)
- Post-Test Facility (PTF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Advanced Photon Source (APS)
- Argonne Leadership Computing Facility (ALCF)

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- | | | |
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| ▪ Katherine Hurst | ▪ Daniel O'Hanlon | |

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RESPONSE TO PREVIOUS YEAR REVIEWERS' COMMENTS

Five reviewers commented on our presentation. We are grateful for their thoughtful comments. Selected excerpts are given below.

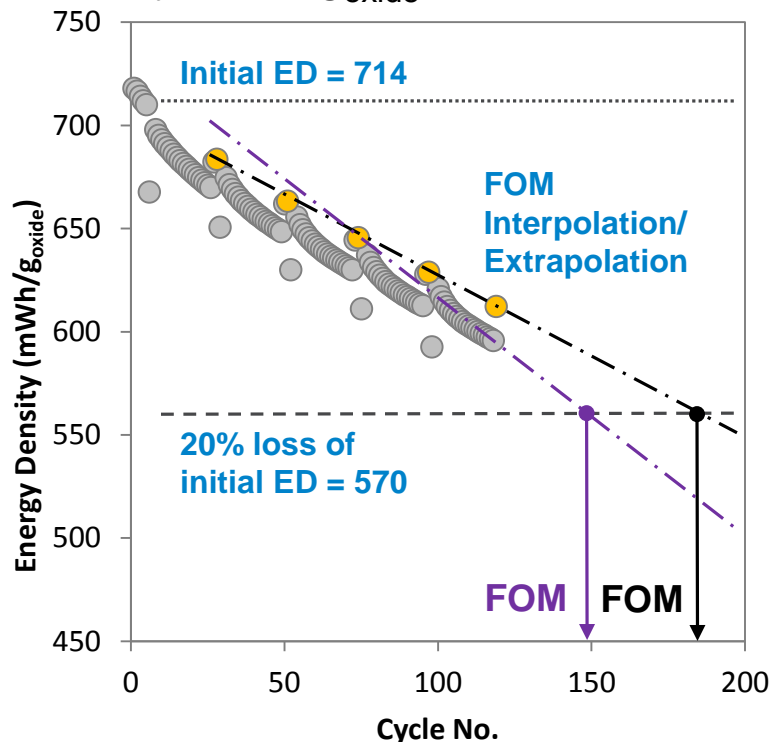
- The reviewers' comments were generally positive.
 - “computational and experimental approach is very well designed”
 - “integrated well with the other team's efforts”
 - “important insights regarding reactions at surfaces of positive and negative electrodes”
- One reviewer indicated that the mechanisms for surface reactions is the novel portion of the work. We agree. Possible surface interactions were probed using closely coupled experimental and computational techniques to determine how functional groups on electrolyte additives influence electrode electrochemical performance and passivation behavior (refer Peebles 2017).
- Another reviewer affirmed the great progress in understanding effects of electrolyte additives on cell impedance and suggested the use of surface techniques to better understand the role of these additives. We agree and point to the use of XPS and SIMS in our experimental efforts. In the past year we have published two articles on mechanisms on some of the additives surveyed in last year's report, including an in-depth analysis of changes to the electrolytes and surfaces with electrolyte aging before use (refer Peebles, 2018).
- One reviewer asked about the “effects of varying the percentage of additives in the matrix”. We have conducted studies that examine this effect. As an example, for a promising combination of additives (VC and TMSPi), a regression model was developed to fit the experimental data in order to obtain an optimized electrolyte formulation (see Sahore 2017).

TECHNICAL BACKUP SLIDES

FIGURE OF MERIT (FOM) METHODOLOGY

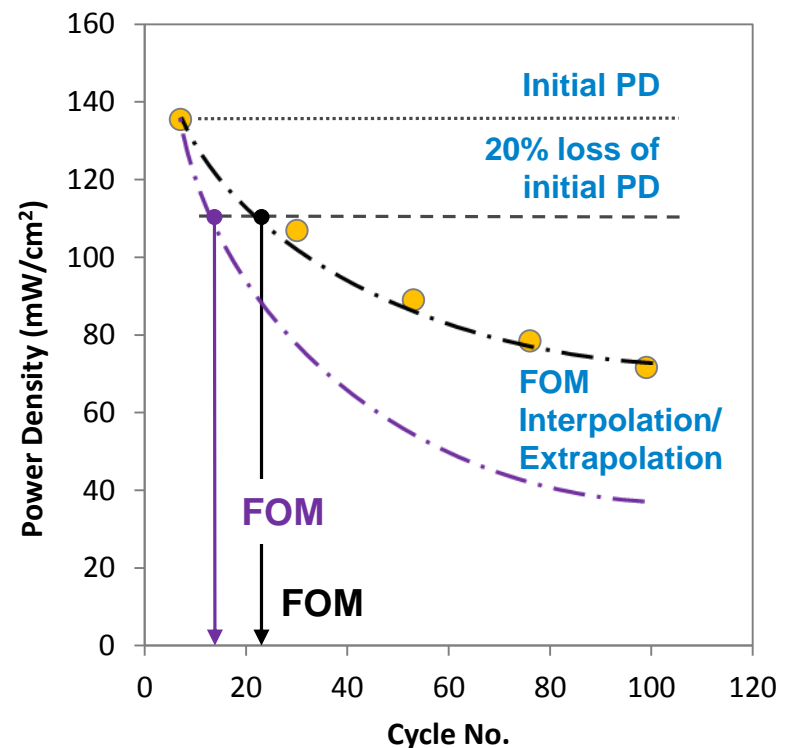
Energy FOM and Power FOM defined

Energy FOM: Number of cycles it takes until 80% of baseline energy density ($\text{Wh/kg}_{\text{oxide}}$) reached



Energy FOM (Baseline): 170

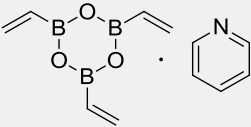
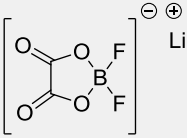
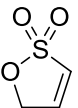
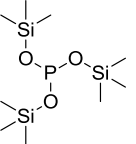
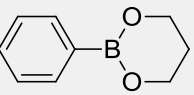
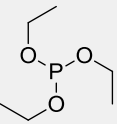
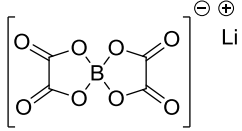
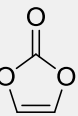
Power FOM: Number of cycles it takes until 80% of baseline power density (mW/cm^2) reached



Power FOM (Baseline): 23

ELECTROLYTE ADDITIVES FOR THE NEGATIVE AND POSITIVE ELECTRODES

Selection rationale based on information in the research literature

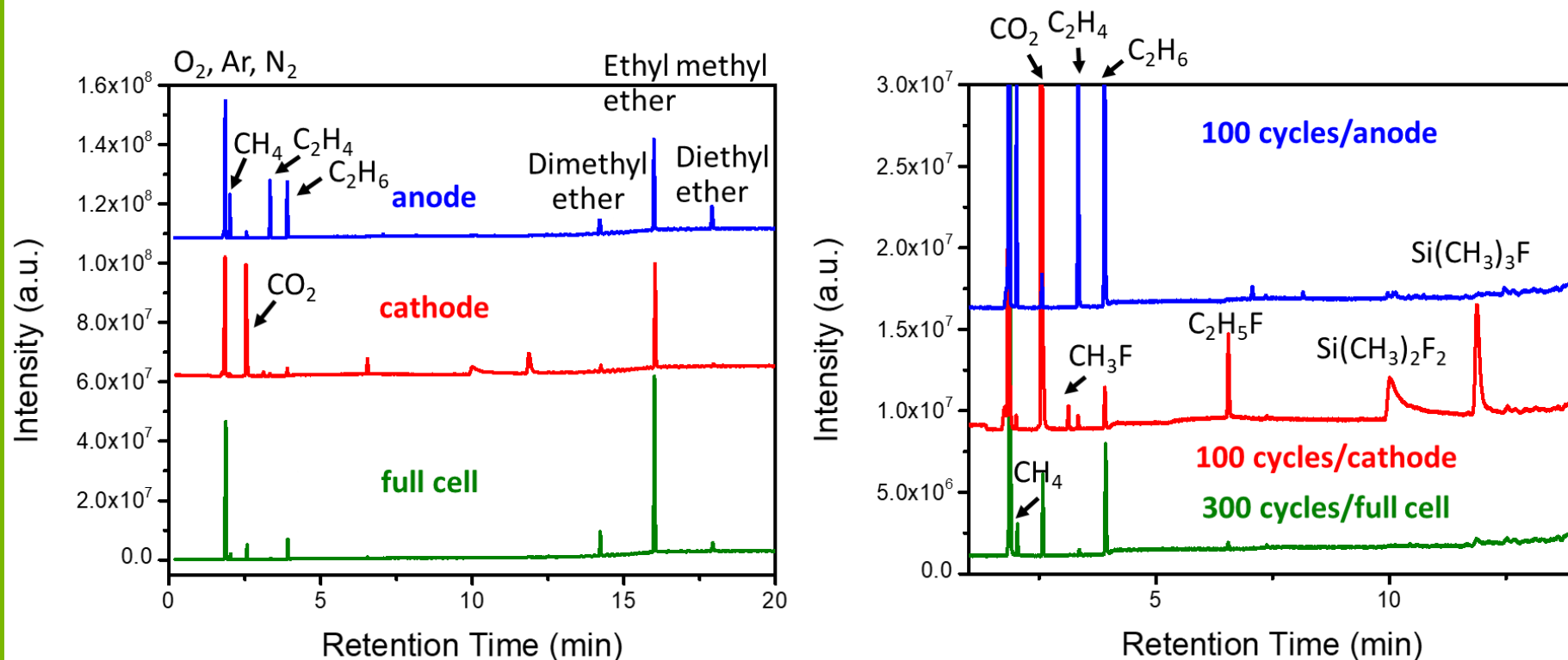
Negative additive	Structure	Wt %	Positive additive	Structure	Wt %
2,4,6-trivinylcyclotriboroxane (tVCBO)		0.25	Lithium difluoro(oxalate)borate (LiDFOB)		2.0
Prop-1-ene-1,3-sultone (PES)		2.0	Tris(trimethylsilyl) phosphite (TMSPI)		1.0
Phenyl boronic acid ethylene glycol ester (PBE)		0.25	Triethyl phosphite (TEPi)		1.0
Lithium bis(oxalato)borate (LiBOB)		1.0			
Vinylene carbonate (VC)		2.0			

Could these compounds help form a robust SEI and lower capacity fade?

Could these compounds “protect the oxide” and lower impedance rise?

SYMMETRIC CELLS ISOLATE REACTIVE GASES.

GC-MS of symmetric Gr//Gr and NMC811//NMC811 pouch cells provides evidence for cross-talk.



- Alkenes generated at the anode react at the cathode.
- CO₂ and fluorocarbons generated at the cathode react at the anode.